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β-[$H_2N(CH_2)_2NH_2$]$_{0.5}$[$ZnHPO_3$], a second modification of ethylenediamine zinc hydrogen phosphite

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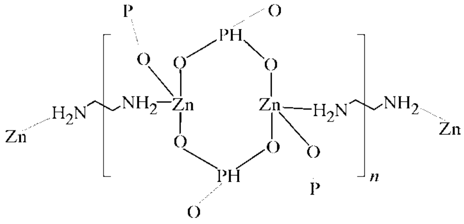
The title compound, poly[dizinc(II)-μ-ethylenediamine-di-μ-(hydrogen phosphito)], β-[$H_2N(CH_2)_2NH_2$]$_{0.5}$[$ZnHPO_3$] or [$Zn_2(HPO_3)_2(C_2H_8N_2)$]$_n$, is a hybrid organic/inorganic solid built up from ethylenediamine molecules (which lie about inversion centres), Zn^{2+} cations (coordinated by three O atoms and one N atom) and HPO_3^{2-} hydrogen phosphite groups. The organic species bond to the Zn atom as unprotonated ligands, acting as bridges between infinite $ZnHPO_3$ layers that propagate as very buckled (001) sheets. The zincophosphite sheets contain polyhedral four- and eight-membered rings in a 4.8^2 topology. β-[$H_2N(CH_2)_2NH_2$]$_{0.5}$·$ZnHPO_3$ complements the previously described α modification of the same stoichiometry [Rodgers & Harrison (2000). *Chem. Commun.* pp. 2385–2386].

Comment

Among the myriad variety of organically templated inorganic networks (Cheetham *et al.*, 1999), a small but distinctive family contains tetrahedral ZnO_3N and pyramidal SeO_3 or pseudo-pyramidal HPO_3 building blocks. The inorganic moieties share vertices, as Zn—O—Se or Zn—O—P bonds, thereby forming an infinite sheet. The linear-chain diamine organic species bonds directly to zinc as a ligand *via* each N atom, thus acting as a 'pillar' between the inorganic sheets. Both modifications of ethylenediamine zinc selenite, [$H_2N(CH_2)_2NH_2$]$_{0.5}$·$ZnSeO_3$ (Choudhury *et al.*, 2002; Millange *et al.*, 2004), contain such sheets of ZnO_3N and SeO_3 groups, fused into a three-dimensional network by the ethylenediamine moieties bonding to the Zn atoms *via* each NH_2 group. These modifications differ in the topological connectivity (O'Keeffe & Hyde, 1996) of the Zn and Se nodal atoms; the first (Choudhury *et al.*, 2002) is based on 6^3 inorganic sheets (each nodal atom participates in three six-membered rings), whereas the second (Millange *et al.*, 2004) contains 4.8^2 sheets. The 1,4-diaminobenzene template in [$C_6N_2H_8$]$_{0.5}$[$ZnHPO_3$] (Kirkpatrick & Harrison, 2004) acts in a similar way to ethylenediamine in the zinc selenite phases; in this case, 6^3 polyhedral sheets built up from ZnO_3N and HPO_3 units arise. Conversely, in [$H_2N(CH_2)_4NH_2$]$_{0.5}$[$ZnHPO_3$] (Ritchie & Harrison, 2004), 4.8^2 polyhedral sheets arise from the ZnO_3N and HPO_3 units. Finally, [$H_2N(CH_2)_2NH_2$]$_{0.5}$[$ZnHPO_3$] (Rodgers & Harrison, 2000; hereafter known as the α modification of this stoichiometry) has a novel structure based on 4.8^2 sheets in which two independent networks form an interpenetrating array akin to some coordination polymers.



(I)

We describe here the title compound, (I), which crystallizes as a second, β, modification of [$H_2N(CH_2)_2NH_2$]$_{0.5}$[$ZnHPO_3$]. Compound (I) (Fig. 1) is built up from neutral unprotonated ethylenediamine [$H_2N(CH_2)_2NH_2$ or $C_2H_8N_2$] molecules, Zn^{2+}

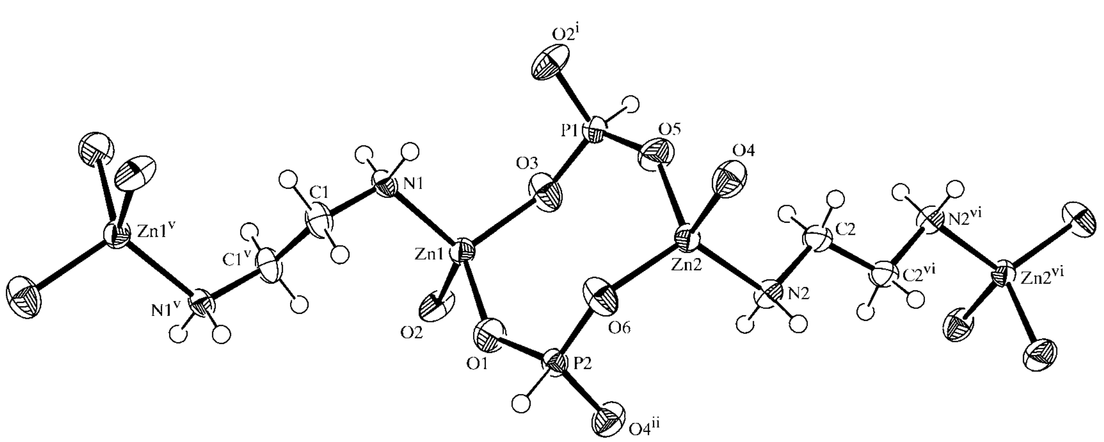


Figure 1
A view of a fragment of (I), showing the different conformations of the N1 and N2 ethylenediamine species. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii. The symmetry codes are as given in Table 1.

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cations and HPO_3^{2-} hydrogen phosphite groups. Each complete ethylenediamine entity is generated from a half-molecule H_2NCH_2– fragment by inversion symmetry. However, these entities differ significantly in their conformations (Table 1); in the N1-containing molecule, atoms Zn1 and $C1^{v}$ (see Table 1 for symmetry code) are *gauche*, whereas in the N2-containing molecule, the equivalent pair of atoms, Zn2 and $C2^{vi}$, are close to *anti*. Both the N atoms of each $H_2N(CH_2)_2NH_2$ molecule make ligand-like bonds to zinc by formal donation of their lone pair of electrons, as observed for the related systems (Rodgers & Harrison, 2000; Kirkpatrick & Harrison, 2004) noted above. The tetrahedral zinc coordination is completed by three O atoms [mean Zn—O = 1.931 (10) Å], each of which form bridges to P atoms of nearby HPO_3^{2-} groups [mean Zn—O—P = 135.1 (6)°]. The pseudo-pyramidal HPO_3^{2-} moieties have typical (Kirkpatrick & Harrison, 2004) geometric parameters, with a mean P—O distance of 1.513 (10) Å and a mean O—P—O angle of 112.9 (7)°. Both distinct HPO_3^{2-} groups form bridges to three nearby zinc cations. As usual, the PH moieties do not interact with any nearby chemical species.

The polyhedral building units in (I) thus consist of ZnO_3N and HPO_3 tetrahedra, linked by way of the O atoms. These units form sheets, built up from strictly alternating Zn- and P-centred moieties, which propagate in the (001) plane. Every tetrahedral node (*i.e.* the Zn and P atoms) participates in one four-atom loop (composed of the asymmetric unit atoms) and two eight-atom loops (Fig. 2), thus generating a 4.8^2 sheet topology (O'Keeffe & Hyde, 1996).

The organic species crosslink the (001) $ZnHPO_3$ sheets in a Zn—*b*—Zn (*b* is the organic bridge) fashion, as shown in Fig. 3, resulting in a hybrid 'pillared' structure in which the inorganic and organic components of the structure alternate along [001]. In principle, this arrangement represents an unusual kind of microporosity, with the channels bounded by both inorganic and organic surfaces. However, in (I), unlike the case of organically pillared zirconyl phosphates (Alberti *et al.*, 1999), the presence of the P—H bond protruding into the channel region and the steric bulk of the ethylenediamine moieties means that there is no possibility of ingress by other chemical species. Finally, the ethylenediamine –NH_2 groups in (I) participate in N—H···O hydrogen bonds (Table 2), all of which are close to linear (mean H—H···O = 172°). These hydrogen bonds appear to help to anchor the organic moiety to an eight-membered ring window in the zinc hydrogen phosphite layer, in a similar way to the behaviour of ethylenediamine in α-$[H_2N(CH_2)_2NH_2]_{0.5}[ZnHPO_3]$ (Rodgers & Harrison, 2000). However, the zincophosphite eight-membered ring pores in (I) are distinctly flattened, whereas in α-$[H_2N(CH_2)_2NH_2]_{0.5}[ZnHPO_3]$ they are far more regular. The recently reported ethylenediammonium zinc hydrogen phosphite $[H_3N(CH_2)_2NH_3][Zn_2(HPO_3)_3]$ (Lin *et al.*, 2004) is a more conventional templated network (Cheetham *et al.*, 1999), in which the organic species is protonated and interacts with the inorganic component by way of N—H···O hydrogen bonds. Interestingly, a 4.8^2 network topology is formed by the $[Zn_2(HPO_3)_3]^{2-}$ sheets.

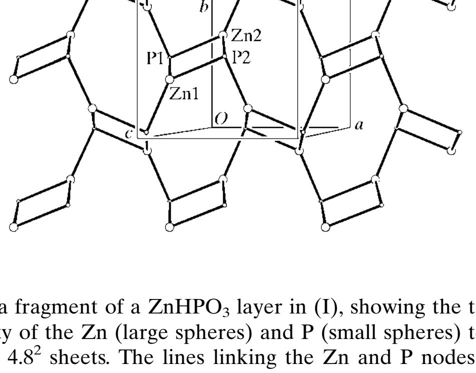

Figure 2
A view of a fragment of a $ZnHPO_3$ layer in (I), showing the topological connectivity of the Zn (large spheres) and P (small spheres) tetrahedral nodes into 4.8^2 sheets. The lines linking the Zn and P nodes represent Zn—O—P bridges, which are not linear (see Table 1).

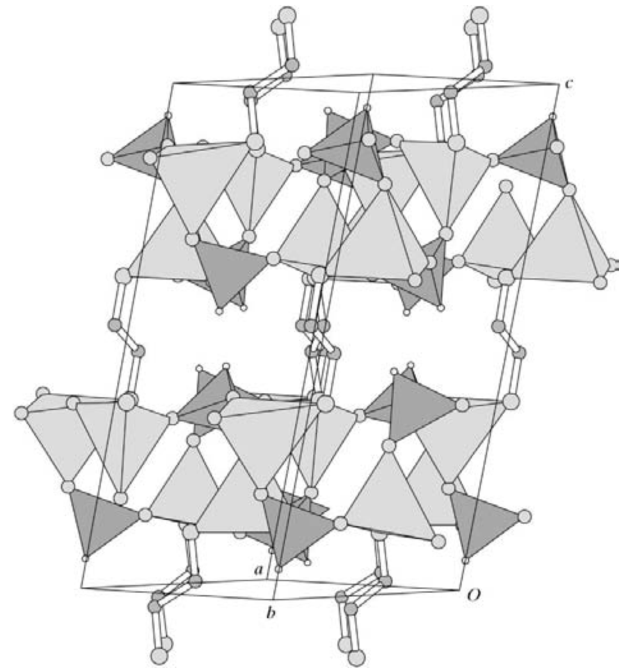

Figure 3
The unit-cell packing in (I), in a polyhedral representation (ZnO_3N groups: light shading; HPO_3 groups: dark shading; ethylenediamine molecules in ball-and-stick representation). All H atoms, except the hydrogen phosphite H1 and H2 species, have been omitted for clarity.

Experimental

A mixture of zinc oxide (3.00 g), phosphorus acid (H_3PO_3, 2.02 g) and ethylenediamine (1.48 g) (molar ratio 2:3:2) was shaken in distilled water (20 ml) in a 60 ml HDPE (high-density polyethylene) bottle for a few minutes, resulting in the formation of a white slurry. The bottle was then placed in an oven at 353 K for 2 d. The solid product was filtered by suction filtration using a Buchner funnel and rinsed with water and acetone, resulting in intergrown fans of needle- and blade-like crystals of (I) accompanied by some undissolved zinc oxide.

Crystal data

$[Zn_2(HPO_3)_2(C_2H_8N_2)]$
$M_r = 350.80$
Monoclinic, $P2_1/c$
$a = 8.3609$ (4) Å
$b = 7.9369$ (4) Å
$c = 15.8259$ (7) Å
$\beta = 104.689$ (1)°
$V = 1015.88$ (8) Å^3
$Z = 4$

$D_x = 2.294$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5099 reflections
$\theta = 2.5$–27.4°
$\mu = 5.04$ mm^{-1}
$T = 293$ (2) K
Slab, colourless
0.33 × 0.30 × 0.11 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{\min} = 0.287$, $T_{\max} = 0.607$
7093 measured reflections

2309 independent reflections
2075 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.031$
$\theta_{\max} = 27.5°$
$h = -10 \rightarrow 8$
$k = -9 \rightarrow 10$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.171$
$S = 1.28$
2309 reflections
128 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0155P)^2 + 26.0795P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.23$ e Å^{-3}
$\Delta\rho_{\min} = -1.01$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0028 (5)

Table 1
Selected geometric parameters (Å, °).

Zn1—O1	1.929 (8)	Zn2—N2	2.021 (8)
Zn1—O3	1.932 (8)	P1—O5	1.497 (8)
Zn1—O2	1.932 (8)	P1—O3	1.518 (9)
Zn1—N1	2.016 (8)	P1—O2$^{\rm i}$	1.519 (7)
Zn2—O6	1.923 (7)	P2—O6	1.511 (8)
Zn2—O5	1.934 (8)	P2—O1	1.513 (8)
Zn2—O4	1.938 (8)	P2—O4$^{\rm ii}$	1.519 (8)
P2—O1—Zn1	141.0 (5)	P2$^{\rm iv}$—O4—Zn2	133.3 (5)
P1$^{\rm iii}$—O2—Zn1	128.8 (5)	P1—O5—Zn2	143.6 (6)
P1—O3—Zn1	134.9 (5)	P2—O6—Zn2	128.9 (5)
Zn1—N1—C1—C1$^{\rm v}$	−64.8 (13)	Zn2—N2—C2—C2$^{\rm vi}$	170.1 (11)

Symmetry codes: (i) $-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (v) $-x, 1-y, 2-z$; (vi) $1-x, 1-y, 1-z$.

Several crystals of (I) were examined, and the diffraction quality was rather poor in all cases, with some peaks showing signs of being 'smeared' or split. All H atoms were placed in idealized locations and refined as riding on their carrier atoms (P—H = 1.32 Å, N—H = 0.90 Å and C—H = 0.97 Å). For all H atoms, the constraint $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(carrier atom) was applied. The maximum difference peak is 1.22 Å from atom H2*A*.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···O3$^{\rm i}$	0.90	2.20	3.099 (11)	173
N1—H1*B*···O4$^{\rm iii}$	0.90	2.10	2.984 (11)	167
N2—H2*A*···O2$^{\rm iv}$	0.90	2.11	2.995 (11)	170
N2—H2*B*···O6$^{\rm ii}$	0.90	2.14	3.038 (12)	177

Symmetry codes: (i) $-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *ORTEP*-3 (Farrugia, 1997) and *ATOMS* (Shape Software, 2003); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1223). Services for accessing these data are described at the back of the journal.

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